Study of Transfer Process of Liquid into and Plasticizer out of Plasticized PVC by Using Short Tests

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Synopsis

When plasticized PVC packagings are put into contact with liquids (blood, food), a migration of plasticizer and additives may occur, being responsible for a contamination of the liquid and a decrease in the mechanical properties of polymer. The interest in short tests is especially pointed out. In contrast to classical real tests, they are not highly time consuming. Moreover, the study of kinetics transfer is easy to complete, because of the constant concentration of liquids in PVC during a short time. A modeling of the transfer process is shown, followed by calculation of the transfer for long real experiments. The model described takes into account both simultaneous transfers, the one concerned with the plasticizer from PVC into liquid and the other with the liquid into the PVC. The study conducted with *n*-heptane as the liquid allows one to understand this complicated transfer problem.

INTRODUCTION

In several applications, a plasticized PVC is in contact with some kind of surrounding medium. Extensively plasticized PVC are used for many biomedical applications such as blood bags, pipes and other blood handling devices.[1] Lower plasticized PVC are used for packaging foodstuffs and cosmetics.[2]

In all cases, plasticized PVC prevents detrimental changes in the packed product due to external influences (oxygen, microorganisms) and to the loss of certain components (water, flavour). But when a plasticized PVC is in contact with the surrounding medium, the plasticizer may stay in place or it may migrate into the liquid with the following results: i- The surrounding medium is contaminated by the plasticizer and additives. Recent reports regarding the possible carcinogenicity of some phthalate plasticizers used in PVC may motivate studies in this field (I). ii- Because of the loss of plasticizer, the polymer shows considerable decrease in mechanical properties.

Studies of these transfers are difficult because of the problems in identifying the migrating species in the presence of chemically complex structures, and the inconvenience of experiments of 6 months or more. Then simulation of real foodstuffs became necessary,[3] and shorter tests were proposed to get the same results for migration: IO d at 45°C, 6 months at 25°C.[4] But studies undertaken on short time experiments showed that simulation conditions (higher temperature, shorter time) could only give a very rough idea of the real life tests, and results did not always correlate.[3-6]

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In fact, it must be said[7] that the migration of additives from plastics into liquid is a complicated problem, and it cannot be described by a single equation derived from the results obtained by only two or three experiments conducted at different temperature values. For several liquids, a double transfer take place simultaneously: plasticizer from plasticized PVC into liquid, and liquid into PVC.[8–10] A knowledge of the transfer kinetics in real situations as well as the effects of such parameters as temperature and percent plasticizer are needed to determine valuable conditions for short tests.

In this work are reported some results on the simultaneous transfer of the liquid into, and plasticizer out of a plasticized PVC when this PVC was contacted with liquid as n-heptane (chosen as simulant for oil by the Food and Drug Administration). The effect of plasticizer percentage on the transfer process was especially studied, by using long real tests and short tests. Short tests were of interest because they were suitable for kinetic studies of the transfer, the concentration of plasticizer and liquid being about constant during the short experiment. Some calculations were done by using a numerically explicit method of finite differences with the results from short tests. These theoretical results were compared with experimental ones obtained with the help of real long tests.

THEORETICAL

A simultaneous diffusion of the liquid takes place into, and the previously dispersed plasticizer out of the PVC. So the loss in plasticizer is directly related to the liquid transfer,[8,11,12] but very often each transfer was studied separately because of the difficulty of the general problem. As a whole, the total above-mentioned transfer is stated to be governed by Fick's laws.

In earlier studies, it was accepted that the concentration of the plasticizer on the PVC face is the same as the concentration in the liquid.[2,7–13] This assumption on the boundary conditions enables the workers to solve the equation of diffusion. But, this concentration of plasticizer is not equal to zero on the PVC face, as it was shown in a recent paper[14] by using attenuated total reflectance studies.

Mathematical Treatment for Short Tests

The classical equation of diffusion with a concentration-dependent diffusivity

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left[D \cdot \frac{\partial_c}{\partial_x}\right] \tag{1}$$

and the above-mentioned boundary condition[14] cannot be solved.

For very short times, the small amount of substance transferred M_t at time t is expressed by the single equation as a function of M_∞ the quantity after infinite time

$$\frac{M_t}{M_\infty} = 4\left(\frac{D \cdot t}{\pi v^2}\right)^{0.5} \tag{2}$$

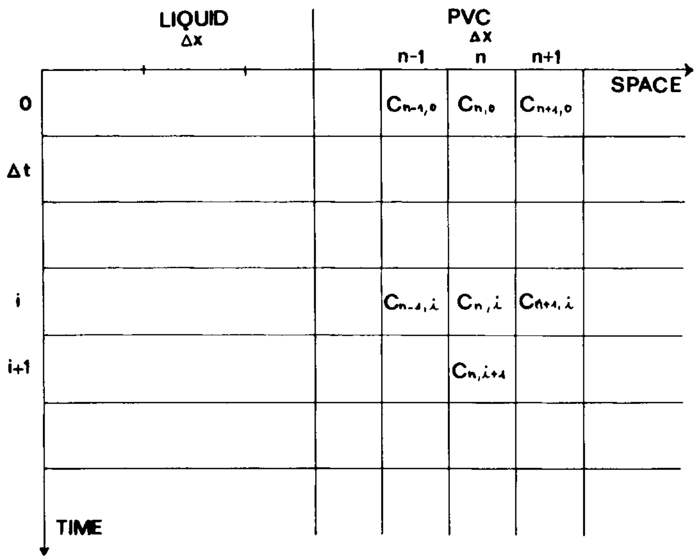

Fig. 1. Diagram space-time for calculation of liquid concentrations with an explicit method with finite differences.

where D is the diffusivity of the substance and x the sheet thickness.

For long times, the solution is given in form of a series for the ratio of the substance transferred M_t/M_∞, as well as for the profile of the concentration of plasticizer developed through PVC sheets, when two assumptions are made: Diffusivity is constant, and the concentration of the plasticizer is 0 on PVC faces.

Numerical Treatment for the Profile of Liquid and the Amount of Liquid Transferred

The problem is solved by using a numerical explicit method with finite differences.

Figure 1 shows the cross section of the PVC sheet of thickness x; the solid is divided into n equal finite slices of thickness Δx by concentration–time reference planes (n,i). The balance of the liquid considered (plasticizer or n-heptane) written on the plane n enables one to conclude that for the liquid

$$C^l_{n,i+1} = \frac{1}{M}\left[C^l_{n-1,i} + (M_l - 2) \cdot C^l_{n,i} + C^l_{n+1,i} \right] \tag{3}$$

with

$$M_l = \frac{(\Delta x)^2}{\Delta t} \cdot \frac{1}{D_l} \tag{4}$$

and

$$D_l = \exp\left(- \frac{A}{C_p + C_l \cdot \alpha} - B \right) \tag{5}$$

$C^l_{n,i+1}$ being the concentration of liquid in PVC at the plane n and time $(i + 1) \cdot \Delta t$. For the plasticizer

$$C^p_{n,i+1} = \frac{1}{M}\left[C^p_{n-1,i} + (M_p - 2) \cdot C^p_{n,i} + C^l_{n+1,i}\right] \quad (6)$$

with

$$M_p = \frac{(\Delta x)^2}{\Delta t} \cdot \frac{1}{D_p} \quad (7)$$

and

$$D_p = \exp\left(-\frac{A'}{C_p + C_l \cdot \beta} - B'\right) \quad (8)$$

$C^p_{n,i+1}$ being the concentration of plasticizer in PVC at the plane n and time $(i + 1) \cdot \Delta t$. In the above equations M_l and M_p are dimensionless moduli concerned with the transfer of liquid and plasticizer.

The diffusivity D_l has been found to act as a function of plasticizer concentration, and the diffusivity D_p was assumed to be a function of the total amount of both liquid and plasticizer situated in the PVC slice.

The concentration of liquids on the PVC faces was obtained by using equations derived from eqs. (3) and (6):

$$C^l_{\text{int},i+1} = \frac{1}{M_l} \cdot \left[C^l_{\text{liq},i} + (M_l - 2) \cdot C^l_{\text{int},i} + C^l_{1,i}\right] \quad (3')$$

$$C^p_{\text{int},i+1} = \frac{1}{M_p} \cdot \left[C^p_{\text{liq},i} + (M_p - 2) \cdot C^p_{\text{int},i} + C^p_{1,i}\right] \quad (6')$$

C^l_{liq} and C^p_{liq} being the concentration of liquid and plasticizer in the liquid. $C^l_{\text{int},i}$ and $C^p_{\text{int},i}$ are the concentration of liquid and plasticizer on the PVC faces at time $i \cdot \Delta t$.

The values of the coefficients A, B, A', B', α, and β depend on the kind of liquid considered, the temperature, and the amount of plasticizer. Our work is in progress in order to give a physical significance to these constants. The total amount of liquid and plasticizer transferred at time t can be easily obtained by integrating the above-mentioned profiles of concentration with respect to time.

EXPERIMENTAL

Materials. Sheets of PVC were prepared with dioctylphthalate (DOP) as plasticizer at different concentrations: 20–28–35.5–50% in weight. These components were blended together in a Plastograph or using a solvent and drying. Sheets were prepared by pressing PVC compounds in a steel mold operated by a press at 150°C for 10 min under a pressure of 50 bars. Disks (18 mm in diam, 3.0 mm thick) were cut from the PVC sheets.

Apparatus for Diffusion. The apparatus and procedure have been described earlier.[15] Experiments for transfer were carried out with PVC disk soaked in *n*-heptane in a closed flask using a controlled rate of stirring.

Analysis of DOP in the liquid was performed by gas chromatography (Intersmat IGC 16), after an addition of dioctyladipate as an internal standard. The weight of the PVC disk was measured at the same time.

These experiments were conducted either as short tests or long real ones. The results enable us to determine the kinetics of both transfers: the liquid into PVC disk and the plasticizer out of the PVC.

Calculation of Profiles of Concentration and Amounts of Liquids Transferred. The profiles of concentration of both liquid and plasticizer developed through the PVC sheet were obtained by using the above-described method with finite differences and kinetic parameter data from short tests. This explicit method allows the use of microcomputer (Micral-R2E, France).

RESULTS

Several parameters are of importance: the stirring of the liquid, the temperature, the plasticizer concentration in PVC, and the kind of liquid.[7]

The experiments were performed in isothermal conditions (30°C) in a well-stirred liquid (the Reynold's number is 3000). The effect of stirring was found to be very important for short times when the transport is controlled by boundary layer phenomena in the liquid phase next to the PVC faces.

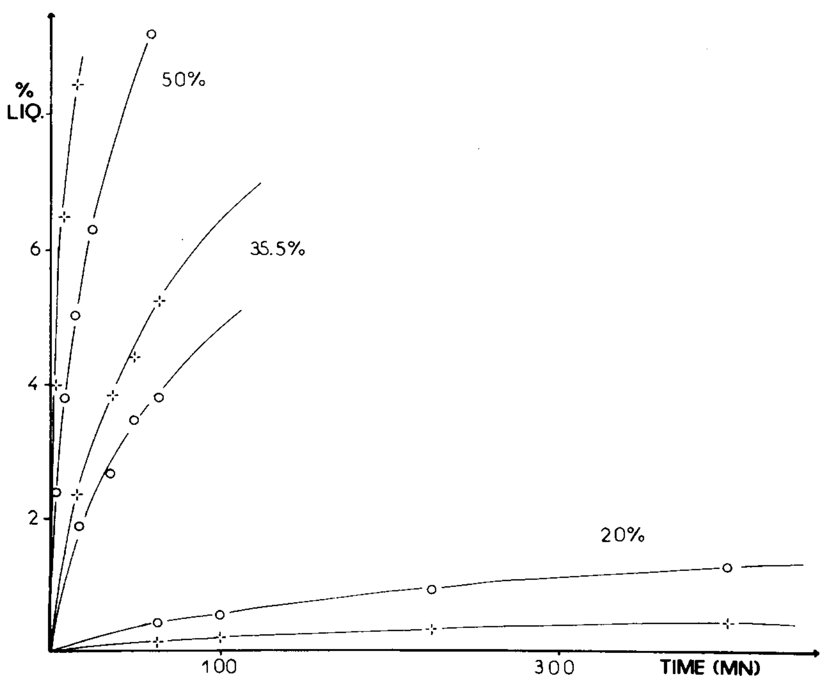

Fig. 2. Short tests. Liquid transfer as a function of time, for different plasticizer concentration in PVC sheets: (+) plasticizer transfer; (○) *n*-heptane transfer.

Several PVC samples with different values for the initial plasticizer concentration were used to study the effect of this concentration on the rate of transfer. *n*-Heptane was chosen for the liquid, because of its common use as simulant for fatty oils according to the suggestion of the Food and Drug Administration.

Kinetics of Transfer Using Short Tests

The values of the concentration of the plasticizer in the liquid and the liquid in the PVC are plotted against the time in Figure 2. For these short tests, the time is short enough so that the amount transferred is very low, and the concentration of plasticizer in PVC is little varied from its initial value.

For the kinetics treatment, the values of the concentrations of liquids are plotted against the square root of the time. As the transfers obeyed Fickian diffusion,[7] straight lines are obtained, as shown in Figure 3. Diffusivities were calculated by using the slope of these straight lines and the amount of liquids transferred at infinite time. These last values were determined with the help of long real tests.

Several relations connecting diffusivities of liquids to the initial concentration of plasticizer were tested. The best results were obtained by relating the logarithm of the diffusivity to the reciprocal of the initial concentration of plasticizer as shown in Figure 4, for the transfer of plasticizer and liquid.

The following values for diffusivity were obtained (Table I) and used for calculation.

In fact, after the soaking of PVC samples in the liquid, the total concen-

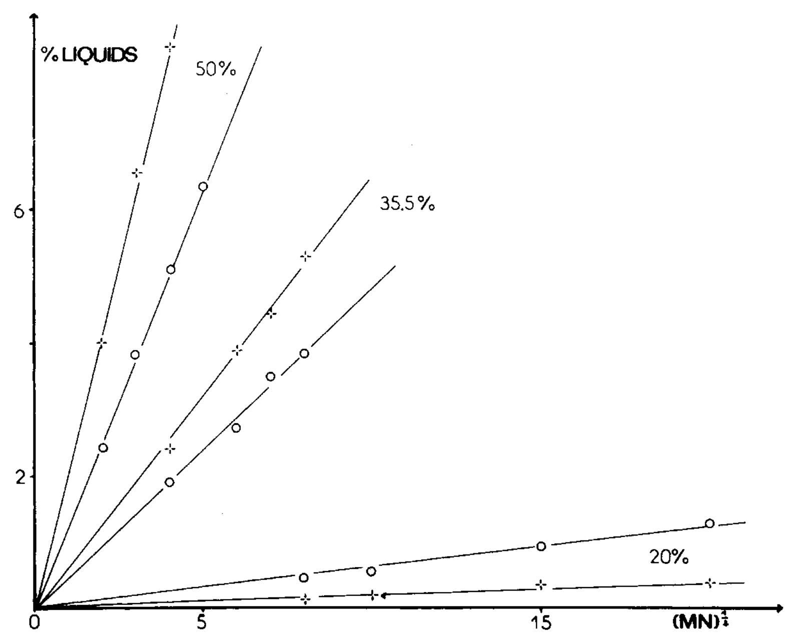

Fig. 3. Short tests. Liquid transfer as a function of the square root of time, for different plasticizer concentration in PVC sheets: (+) plasticizer transfer; (○) *n*-heptane transfer.

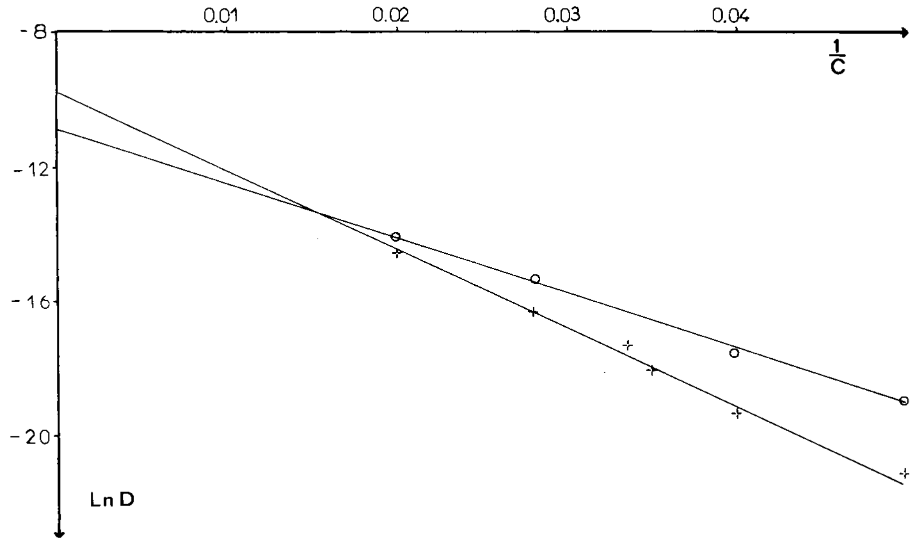

Fig. 4. log D as a function of reciprocal of plasticizer concentration in PVC sheets: (+) plasticizer transfer; (○) n-heptane transfer.

tration of both plasticizer and n-heptane must be considered, and the denominator of the equations for diffusivity contains the sum of these concentrations. [eqs. (5) and (6)]. The coefficients α and β in eqs. (5) and (8) are not equal to 1 when the best results are desired, although the total liquid (plasticizer and n-heptane) is concerned in these above equations. Up to now, no quite satisfactory explanation can be given for this fact. It is perhaps due to the different physical properties of plasticizer and n-heptane: diffusivity, viscosity, and molecular size.

Long Real Tests: Experiment and Calculation

The calculated profiles of concentration of plasticizer developed through the PVC sheet at different times are shown in Figure 5. These profiles are about the same as those obtained in previous works[11,15] with methanol and benzyl alcohol used as the liquid. The concentration on the face was not equal to zero as it was previously determined[14] by using attenuated total reflectance measurements on PVC faces.

The profiles of concentration simultaneously calculated for n-heptane through the PVC sheet are shown in Figure 6.

Another interesting result is shown in Figure 7, where the amount of

TABLE I
Diffusivity Coefficients and Parameters for Computerization

$\log D_p = -\frac{234}{C_p} - 9.7$	$\log D_l = -\frac{160}{C_l} - 10.9$
$\log D_p = -\frac{234}{C_p + 1.6C_l} - 9.7$	$\log D_l = -\frac{160}{C_p + 0.1C_l} - 10.9$
$\Delta x = 3.0 \times 10^{-2}$ cm	$\Delta t = 360$ s

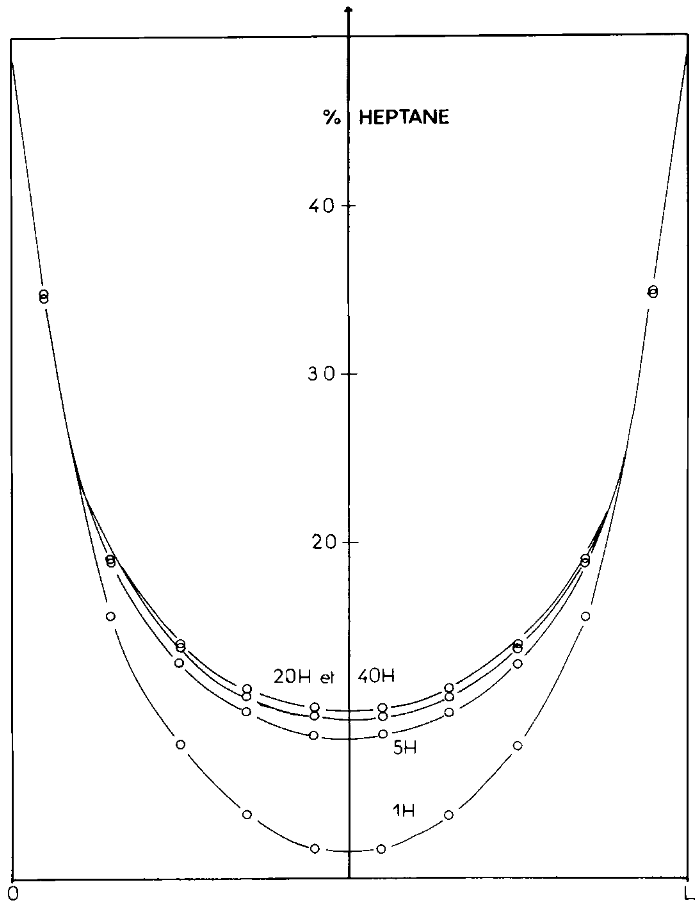

Fig. 5. Long real tests. Profiles of concentration of plasticizer developed through PVC sheets. Plasticizer percentage = 50%, temperature = 30°C.

plasticizer transferred into the liquid is plotted against the time. The calculated values are about the same as the experimental ones, and this for different times. In Figure 7 the kinetics results from experiments and calculation can be compared for the transfer of plasticizer and n-heptane. This is a proof of the validity of the present method of calculation, because the amounts of plasticizer and liquid transferred are obtained by using the profiles of plasticizer and liquid calculated by the same method.

CONCLUSIONS

As the earlier studies were highly time-consuming (several weeks or months), our present work has been aimed in reducing the lengths of time of investigation. Moreover, these short tests enable us to study in a better way the kinetics of simultaneous transfers of both the plasticizer and liquid, because the concentration of these liquids in the PVC can be considered as constant during the short experiment. Some expressions relating diffusivity to the concentrations of plasticizer and liquid are proposed and tested. The use of an explicit method with finite differences enabled us to calculate the

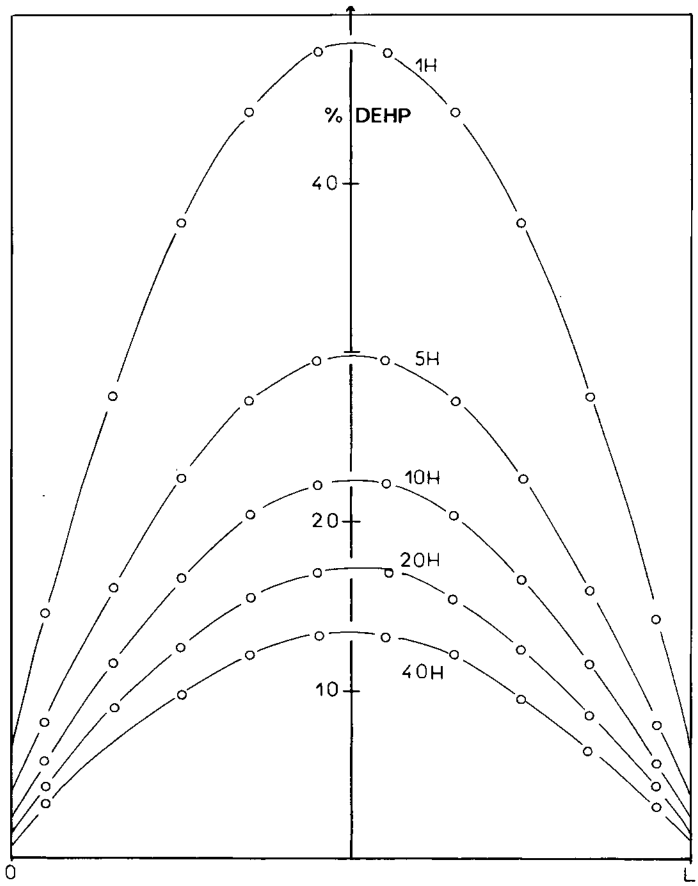

Fig. 6. Long real tests. Profiles of concentration of n-heptane developed through PVC sheets. Plasticizer percentage = 50%, temperature = 30°C.

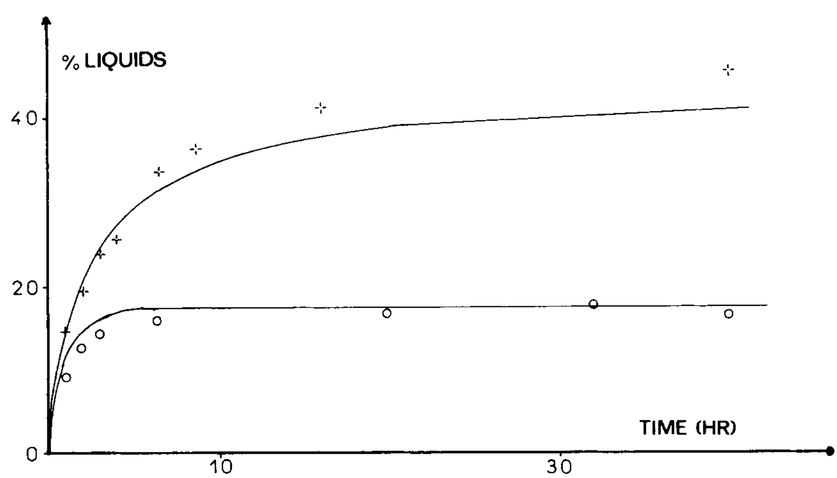

Fig. 7. Long real tests. Kinetics of transfer of plasticizer out of, and n-heptane into, the PVC. Plasticizer percentage = 50%, temperature = 30°C.

profiles of concentrations of n-heptane and plasticizer developed through the PVC sheet, as well as the kinetics of transfer of these liquids. These calculated kinetics of transfer were found to be in good agreement with the experimental ones. Also, the calculated values of the plasticizer concentration obtained on PVC faces were about the same as those determined by attenuated total reflectance measurements.

APPENDIX: NOMENCLATURE

A, B, α	constant coefficients in eq. (5) for the diffusivity of n-heptane
A', B', β	constant coefficients in eq. (8) for the diffusivity of plasticizer
$C^p_{n,i}$	concentration of plasticizer in PVC at plane n and time $i\Delta t$
$C^l_{n,i}$	concentration of liquid in PVC at plane n and time $i\Delta t$
$C^l_{\text{int},i}$	concentration of liquid on PVC faces at time $i\Delta t$
D_l, D_p	diffusivity of liquid and plasticizer, respectively
M_t	amount of liquid transferred at time t
M_∞	amount of liquid transferred at infinite time
M_l, M_p	dimensionless modulus for the liquid and plasticizer
Δx	increment of space
Δt	increment of time

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